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(54) Manufacture of Fume Silica

(57) Highly disperse fume silica is manufactured by flame hydrolysis, wherein vaporised combustible silicon compounds and oxygen-containing gas preheated to at least 100°C are mixed with water vapour prior to introduction into the combustion chamber.

hexa methyl disiloxane

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SPECIFICATION
Manufacture of Fume Silica

The present invention relates to a process for the manufacture of fume silica by flame hydrolysis.

Very finely divided silica (highly disperse silica) may be manufactured by flame hydrolysis, which comprises reacting a gaseous or vaporisable silicon compound and, optionally, another gas that will burn to form water, with oxygen in a flame (see, for example, DE 900 339, U.S. 2 399 687, G.B. 17325/77 Serial No. 1562966 (equivalent to DE 26 20 737 Al)). Silica manufactured in this manner is known as pyrogenic silica or fume silica. Satisfactory results can be obtained by this method when silicon tetrachloride is used as the gaseous silicon compound. It is, however, often advantageous to use an organosilane as the gaseous silicon compound, but the silica produced from these compounds tends to be contaminated with carbon and thus tends to be dark in colour. This result when using silicon compounds containing silicon-bonded organic groups, especially halogen-containing silicon compounds, has previously been counteracted by using an additional fuel, namely an additional gas that will burn to form water, for example hydrogen or a hydrocarbon.

G.B. 17325/77 Serial No. 1562966 describes and claims a process for the manufacture of fume silica, which comprises the steps of:

(i) feeding a liquid organosilane, preferably tetramethylsilane or a methylchlorosilane, into an evaporation vessel at such a rate that the liquid level within the said vessel remains substantially constant;

(ii) evaporating the liquid organosilane within the said vessel under a pressure within the range of from 0.2 to 1.2, preferably 0.4 to 0.9, atmospheres gauge and at a temperature of not more than 45 deg C, preferably from 20 to 35 deg C, above the boiling point of the organosilane at 760 torr;

(iii) maintaining the resulting gaseous organosilane at the said temperature until it is

(iv) mixed with a gas comprising at least 15% by volume of oxygen, preferably air, and, optionally, with a gas (other than a gaseous organosilane) that will burn to form water, preferably hydrogen, water gas, town gas, methane, propane or methanol;

(v) feeding the resulting gas mixture into a combustion chamber *via* a conical inlet nozzle, while

(vi) feeding additional oxygen-containing gas into the combustion chamber *via* an annular nozzle surrounding the conical inlet nozzle;

(vii) combusting the gas mixture within the combustion chamber at a temperature of at least 1100°C, while

(viii) cooling the combustion chamber by means of an indirect positive cooling means.

The present invention provides a process for the manufacture of fume silica, which comprises the steps of:

(i) feeding a liquid combustible silicon compound into an evaporation vessel at such a rate that the liquid level within the said vessel remains substantially constant;

(ii) evaporating the liquid silicon compound within the said vessel under a substantially constant vapour pressure and at a substantially constant temperature;

(iii) maintaining the resulting gaseous silicon compound at the said temperature until all the reactants have been mixed together;

(iv) mixing the gaseous silicon compound with an oxygencontaining gas that has been preheated to a temperature of at least 100°C; and, simultaneously or subsequently,

(v) mixing the gaseous silicon compound with water vapour;

(vi) feeding the resulting gaseous silicon compound/oxygen-containing gas/water vapour mixture into a combustion chamber *via* a conical inlet nozzle, while

(vii) feeding additional oxygen-containing gas into the combustion chamber *via* an annular nozzle surrounding the conical inlet nozzle; and

(viii) combusting the gas mixture within the combustion chamber; while

(ix) cooling the combustion chamber by means of indirect forced cooling.

The process according to the invention does not require the use of additional fuels that burn to form water and thus results in the saving of large quantities of such fuels. Moreover, the addition of water vapour to the gaseous silicon compound/oxygen-containing gas mixture surprisingly does not adversely affect the quality of the product or the duration of operation of the apparatus and, in particular, does not result in the conical inlet becoming obstructed by deposited silica.

Combustible silicon compounds that may be used in the present process are those gaseous and/or vaporisable combustible silicon compounds that have been or could be used in previous flame-hydrolysis processes for the manufacture of fume silica, optionally in conjunction with additional gases that burn to form water.

The process according to the invention can be used for reacting combustible silicon compounds having boiling points (without substantial decomposition) of up to 200°C (as measured at normal pressure), or mixtures thereof, in order to form high-purity highly disperse fume silica. Such compounds include organochlorosilanes, hydrogenchlorosilanes, hydrogenorganosilanes (that is without any substituents other than organic groups), and silanols and siloxanes in which any silicon valencies not satisfied by oxygen atoms are satisfied by hydrogen atoms, chlorine atoms or organic groups.

Tetramethylsilane, methyltrichlorosilane and trichlorosilane, individually or in admixture, are preferably used as the combustible silicon compound, but examples of other suitable

combustible silicon compounds include silane, disilane, trisilane, tetrasilane; trichlorosilane, dichlorosilane, chlorosilane; methylsilane, dimethylsilane, trimethylsilane, tetramethylsilane; methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane; methylchlorosilane, methyldichlorosilane, dimethylchlorosilane; hexamethyldisilane, tetramethyldisilane; pentamethylchlorodisilane, trimethyltrichlorodisilane, dimethyltetrachlorodisilane; and silanes of the formula

$$Cl[Si(CH_3)_2]_n$$

in which n ~~denotes an integer from~~ 2 to 8; disiloxane, hexamethyldisiloxane; and trimethylsilanol. ~~A mixture of~~ two or more combustible silicon compounds may be used.

Some of the combustible silicon compounds that may be used in the process according to the invention are compounds that are otherwise not useful or cannot otherwise be used in the quantities in which they are produced. Such compounds have previously had to be treated as waste, which is disadvantageous both economically and environmentally. Such compounds are, for example, those obtained as by-products, for example as first and last runnings, in the distillative separation of products from the Müller-Rochow synthesis, in which silicon or a silicon alloy is reacted with hydrogen chloride or an organic halide (especially methyl chloride) to produce a chlorosilane or an organochlorosilane. For use in the present process, such first and last runnings do not need to be separated further, but they should preferably not contain any solids such as carbon. The main products of the Müller-Rochow synthesis may also be used in the present process.

In carrying out the process according to the invention, the combustible silicon compound, or mixture thereof, is fed in liquid form into an evaporation vessel at such a rate that the liquid level within the vessel remains substantially constant, for which purpose the feed rate of the liquid silicon compounds should, of course, be the same as the evaporation rate (expressed in weight per unit time). The silicon compound is advantageously evaporated within the said vessel under a vapour pressure within the range of from 1.2 to 2.2 bar, preferably from 1.4 to 2.0 bar (absolute) and advantageously at a temperature of not more than 50 deg C above the boiling point of the combustible silicon compound (or above the boiling range of the mixture of such compounds) at 760 torr, preferably at a temperature within the range of from 20 to 35 deg C above the said boiling point (or boiling range). Heating of the heated surface (or heat-emitting surface) within the evaporation vessel may be effected, for example, by means of a heating liquid (for example hot water at a temperature within the range of from 95 to 100°C), by means of water vapour (optionally superheated under pressure to up to 250°C), or by electrical means.

The temperature of the gaseous combustible silicon compound must be maintained substantially at the evaporation temperature until all the reactants have been mixed together, in order to prevent any condensation of the said silicon compound. This may be achieved, for example, by protecting the pipe through which the said silicon compound passes from the evaporation vessel to the combustion chamber against heat-radiation by means of a heat-insulating material, by providing the said pipe with a heating jacket through which hot water at a temperature within the range of from 95 to 100°C or water vapour (optionally superheated under pressure to up to 250°C) is passed, or by electrical heating.

The gaseous combustible silicon compound is subsequently mixed, while being maintained at said temperature, with an oxygen-containing gas. This oxygen-containing gas, by which is meant a gas containing free oxygen, advantageously comprises at least 15% by volume of oxygen. It may consist of pure oxygen or of a mixture of oxygen and a gas that is inert toward the reactants, preferably nitrogen or one of the inert/rare/noble gases. Preferably the oxygen-containing gas is air.

Prior to being mixed with the gaseous combustible silicon compound, the oxygen-containing gas has been preheated to a temperature of at least 100°C, advantageously to a temperature within the range of from 100 to 700°C, preferably from 150 to 400°C. The temperature of the oxygen-containing gas should, in any case, be sufficiently high that the gaseous combustible silicon compound does not liquefy on being mixed with the oxygen-containing gas.

Simultaneously with, or subsequently to, the mixing of the gaseous combustible silicon compound with the oxygen-containing gas, water vapour is mixed with the gaseous combustible silicon compound. The mixing of the water vapour with the gaseous combustible silicon compound must not take place prior to, that is upstream of, the mixing of the oxygen-containing gas, or a portion thereof, with the gaseous combustible silicon compound. Preferably, the oxygen-containing gas and the water vapour are simultaneously mixed with the gaseous combustible silicon compound. This may be effected by bringing the three gases separately to the same point, or by premixing the oxygen-containing gas and the water vapour and then mixing this premixture with the gaseous combustible silicon compound.

Prior to being mixed with the oxygen-containing gas and the gaseous combustible silicon compound, the water vapour has advantageously been preheated to substantially the same temperature as that to which the oxygen-containing gas has been preheated. The water vapour may, however, be at a temperature higher or lower than that of the oxygen-

containing gas but it should, of course, be at a temperature that is sufficiently high to prevent both the water and the silicon compound from precipitating.

The amount of oxygen-containing gas used should be such that all Si-H bonds and all Si-organic bonds are oxidised to Si-O bonds and that any organic radicals present are completely combusted to colourless gaseous products. The amount of water vapour used should be such that all other silicon bonds are hydrolysed to Si-O bonds.

Advantageously, the oxygen-containing gas is used, in this stage of the process, in an excess of at least 5% by weight, preferably an excess of from 10 to 50% by weight, based on the stoichiometric amount of oxygen relative to all oxidisable compounds and/or groups present.

The mixing of the gaseous components may be effected in a part of the apparatus that is part of the burner in which the combustion chamber is situated, for example mixing (or the last mixing step when mixing is effected in two steps) may be effected immediately upstream of the conical inlet nozzle through which the gas mixture enters the combustion chamber. This conical inlet nozzle advantageously has an internal diameter, at its opening into the combustion chamber, of from 20 to 100 mm, preferably from 50 to 70 mm. It is surrounded by an annular nozzle (a flushing nozzle), which advantageously has a width within the range of from 0.2 to 2 mm, through which additional oxygen-containing gas is introduced into the combustion chamber. A suitable nozzle arrangement is described and illustrated in G.B. 17325/77 Serial No. 1562966 and DE 26 20 737 Al.

The amount of oxygen-containing gas introduced through this annular nozzle is advantageously an additional excess of from 5 to 15% by weight, preferably about 10% by weight, based on the stoichiometric amount of oxygen as defined above. This additional oxygen-containing gas is advantageously also preheated to a temperature of at least 100°C, preferably from 100 to 700°C, and especially from 150 to 400°C, prior to being fed into the combustion chamber and mixed with the gas mixture issuing from the conical inlet nozzle. Moreover, this additional oxygen-containing gas is also advantageously premixed with additional water vapour prior to being mixed with the said gas mixture. The amount of additional water vapour used here is advantageously from 5 to 20% by weight, based on the stoichiometric amount of water vapour, and this additional water vapour is also advantageously preheated to the same temperature as that to which the other water vapour is preheated.

The final gas mixture, consisting of the gas mixture issuing from the conical inlet nozzle and the gas or gas mixture issuing from the annular nozzle and comprising the gaseous combustible silicon compound, the water vapour and the oxygen-containing gas, is burnt in a flame in the combustion chamber, thus producing a large amount of heat, which is conducted away by means of indirect forced cooling means. This cooling may be effected by cooling the combustion chamber externally by means of a jacket through which a coolant is circulated, for example water or, preferably an oxygen-containing gas, especially air, which may subsequently, after heating or cooling as necessary, be used as the oxygen-containing gas in the reaction.

The overall volumetric ratios of the three gaseous components is not critical, but these ratios are advantageously so regulated that the flame temperature is within the range of from 800 to 1400°C.

Fume silica manufactured according to the present process is generally in the form of highly disperse silica having an average particle size of less than 1 μm and a BET specific surface area within the range of from 50 to 450 m²/g, especially from 100 to 400 m²/g. (The term "BET specific surface area" means the specific surface area as determined by nitrogen adsorption according to the method given in ASTM Special Technical Publication No. 51 (1941) pages 95—105, which is usually known as "the BET method".) It is, for example, suitable for use in thickening both polar and non-polar liquids and also as a reinforcing filler, especially in organopolysiloxane compositions curable to elastomers (which may, for example, be heat-vulcanisable compositions containing peroxidic crosslinking agents, one-component or two-component room-temperature-vulcanisable compositions, or composition in which crosslinking is achieved by adding silicon-bonded hydrogen to aliphatic multiple bonds), and in general it is suitable for all applications for which finely divided fume silica has previously been used.

The following examples illustrate the process of the invention. (All volumes specified are measured at standard temperature and pressure. All pressures specified are absolute pressures.)

Example 1

Liquid methyltrichlorosilane was fed into an evaporator at a rate of 25 kg/h under a pressure of 2.5 bar by means of a diaphragm piston pump. The evaporator had a heat-radiating surface which had a surface area of 0.5 m² and was heated by means of water vapour under a pressure of 1.5 bar. The flow of the water vapour was controlled by means of a "Samson" (Trade Mark) regulator, which itself was controlled by the vapour pressure of the methyltrichlorosilane in the evaporator in such a manner that the said vapour pressure was maintained at 1.5 bar and that the liquid level of the methyltrichlorosilane was held constant. The temperature in the evaporator was about 78°C.

The gaseous methyltrichlorosilane was passed from the evaporator to a burner nozzle via a pipe provided with a jacket through which water

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vapour flowed under a pressure of 1.5 bar and also provided with a regulating device to maintain a constant temperature.

Immediately upstream of the burner nozzle the gaseous methyltrichlorosilane (25 kg/h) was mixed with 100 m³/h of air having a temperature of about 200°C and with approximately 10 kg/h of water vapour. The resulting gas mixture was fed through the conical nozzle 11 of the nozzle arrangement shown in the drawings accompanying G.B. 17325/77 and DE 28 20 737 Al, having an opening/orifice 12 with an internal diameter of 50 mm. The burner orifice was acute-angled and thin-walled.

8 m³/h of air enriched with water vapour were fed through the annular nozzle 14 (width 0.5 mm) which surrounds the conical nozzle 11 in the said nozzle arrangement.

The gas mixture issuing from the nozzle arrangement was burnt in a flame below the nozzle arrangement in a combustion chamber having a length of 350 cm and a diameter of 60 cm and surrounded by a 5 cm-wide jacket through which air at an initial temperature of about 20°C was sucked at a rate of 800 m³/h. The air had a temperature of about 120°C on leaving the jacket and 100 m³/h of this hot air was used, after further heating, as the air for the reaction.

Highly transparent highly disperse fume silica was obtained, which had an average particle size of less than 1 μm and a BET specific surface area of 188 m²/g.

Example 2

The procedure of Example 1 was repeated with the variations that 22 kg/h of trichlorosilane were used (instead of 25 kg/h of methyltrichlorosilane) and that the amount of air was 90 m³/h (instead of 100 m³/h).

Highly transparent highly disperse fume silica having a BET specific surface area of 395 m²/g was obtained.

Example 3

The procedure of Example 1 was repeated with the variations that 25 kg/h of methyldichlorosilane were used (instead of 25 kg/h of methyltrichlorosilane) and that the amount of air was 130 m³/h (instead of 100 m³/h).

Highly disperse fume silica having a BET specific surface area of 187 m²/g was obtained.

Example 4

The procedure of Example 1 was repeated with the variations that 25 kg/h of a mixture of 50% by volume of methyltrichlorosilane and 50% by volume of trichlorosilane were used (instead of 25 kg/h of methyltrichlorosilane) and that the amount of air was 64 m³/h (instead of 100 m³/h).

Highly disperse fume silica having a BET specific surface area of 278 m²/g was obtained.

Example 5

The procedure of Example 1 was repeated with the variations that:

(i) 25 kg/h of a mixture of combustible silicon compounds obtained as a first running in the distillation of the crude product from a Müller-Rochow synthesis in which the starting material was methyl chloride, which mixture comprised (as determined by gas chromatography) trichlorosilane, methyldichlorosilane, dimethylchlorosilane, tetramethylsilane, other silanes and hydrocarbons (instead of 25 m³/h of methyltrichlorosilane);

(ii) that the vapour pressure in the evaporator was 1.8 bar (instead of 1.5 bar);

(iii) that the temperature in the evaporator and connecting pipe was higher than 60°C;

(iv) that the connecting pipe was heated electrically (instead of by means of water vapour flowing through a heating jacket);

(v) that the amount of air was 110 m³/h (instead of 100 m³/h);

(vi) that the 10 kg/h of water vapour had a temperature of about 150°C; and

(vii) that the 8 m³/h of air issuing from the annular nozzle was mixed with 5 kg/h of water vapour at about 140°C.

Fume silica having an average particle size of less than 1 μm and a BET specific surface area of 164 m²/g was obtained.

Example 6

The procedure of Example 5 was repeated with the variation that:

(i) 25 kg/h of a mixture of combustible silicon compounds obtained as a last running (instead of a first running) in the distillation of the crude product from a Müller-Rochow synthesis in which the starting material was methyl chloride, which mixture comprised (as determined by gas chromatography) dimethyldichlorosilane, ethylmethyldichlorosilane, tetramethyldichlorosiloxane, dimethyltetrachlorodisilane, other volatile silicon compounds and hydrocarbons;

(ii) that the vapour pressure in the evaporator was 2.0 bar (instead of 1.8 bar);

(iii) that the temperature in the evaporator and connecting pipe was higher than 140°C;

(iv) that the amount of air was 100 m³/h (instead of 110 m³/h);

(v) that the amount of water vapour was 20 kg/h (at 150°C) (instead of 10 kg/h);

(vi) that the 5 kg/h of water vapour mixed with the air issuing from the annular nozzle had a temperature of about 120°C.

Fume silica having an average particle size of less than 1 μm and a BET specific surface area of 196 m²/g was obtained.

Claims

1. A process for the manufacture of fume silica, which comprises the steps of:

(i) feeding a liquid combustible silicon compound into an evaporation vessel at such a

rate that the liquid level within the said vessel remains substantially constant;

(ii) evaporating the liquid silicon compound within the said vessel under a substantially constant vapour pressure and at a substantially constant temperature;

(iii) maintaining the resulting gaseous silicon compound at the said temperature until all the reactants have been mixed together;

(iv) mixing the gaseous silicon compound with an oxygen-containing gas that has been preheated to a temperature of at least 100°C; and, simultaneously or subsequently,

(v) mixing the gaseous silicon compound with water vapour;

(vi) feeding the resulting gaseous silicon compound/oxygen-containing gas/water vapour mixture into a combustion chamber *via* a conical inlet nozzle, while

(vii) feeding additional oxygen-containing gas into the combustion chamber *via* an annular nozzle surrounding the conical inlet nozzle; and

(viii) combusting the gas mixture within the combustion chamber; while

(ix) cooling the combustion chamber by means of indirect forced cooling.

2. A process as claimed in claim 1, wherein the combustible silicon compound or compounds has or have a boiling point not exceeding 200°C.

3. A process as claimed in claim 1 or claim 2, wherein the combustible silicon compound or compounds comprise(s) an organochlorosilane, a hydrogenchlorosilane, a hydrogenorganosilane, and/or a silanol or siloxane in which any silicon valencies not satisfied by oxygen atoms are satisfied by hydrogen atoms, chlorine atoms or organic groups.

4. A process as claimed in claim 1, wherein the combustible silicon compound comprises tetramethylsilane, methyltrichlorosilane and/or trichlorosilane.

5. A process as claimed in any one of claims 1 to 4, wherein the liquid silicon compound is evaporated under a vapour pressure within the range of from 1.2 to 2.2 bar.

6. A process as claimed in claim 5, wherein the liquid silicon compound is evaporated under a vapour pressure within the range of from 1.4 to 2.0 bar.

7. A process as claimed in any one of claims 1 to 6, wherein the liquid silicon compound is evaporated at a temperature of not more than 50 deg C above its boiling point at 760 torr.

8. A process as claimed in claim 7, wherein the liquid silicon compound is evaporated at a temperature within the range of from 20 to 35 deg C above its boiling point at 760 torr.

9. A process as claimed in any one of claims 1 to 8, wherein the oxygencontaining gas comprises at least 15% by weight of oxygen.

10. A process as claimed in any one of claims 1 to 9, wherein the oxygen-containing gas comprises a mixture of oxygen and nitrogen or a noble gas.

11. A process as claimed in claim 10, wherein the oxygen containing gas is air.

12 A process as claimed in any one of claims 1 to 11, wherein the oxygen-containing gas has been preheated to a temperature within the range of from 100 to 700°C.

13. A process as claimed in claim 12, wherein the oxygen-containing gas has been preheated to a temperature within the range of from 150 to 400°C.

14. A process as claimed in any one of claims 1 to 13, wherein the oxygen-containing gas and the water vapour are simultaneously mixed with the gaseous silicon compound.

15. A process as claimed in any one of claims 1 to 14, wherein, prior to being mixed with the gaseous silicon compound, the water vapour has been preheated to substantially the same temperature as that to which the oxygen-containing gas has been preheated.

16. A process as claimed in any one of claims 1 to 15, wherein the oxygen-containing gas is initially mixed with the gaseous silicon compound in an amount constituting an excess of at least 5% by weight, based on the stoichiometric amount of oxygen relative to all oxidisable compounds and/or groups present.

17. A process as claimed in claim 16, wherein the oxygen-containing gas is initially mixed with the organosilane in an amount constituting an excess of from 10 to 50% by weight, based on the stoichiometric amount of oxygen relative to all oxidisable compounds and/or groups present.

18. A process as claimed in claim 16 or claim 17, wherein the additional amount of the oxygen-containing gas fed through the annular nozzle is an amount constituting an additional excess of from 5 to 15% by weight, based on the stoichiometric amount of oxygen relative to all oxidisable compounds and/or groups present.

19. A process as claimed in any one of claims 1 to 18, wherein the additional oxygen-containing gas has been preheated to a temperature of at least 100°C prior to being fed into the combustion chamber.

20. A process as claimed in claim 19, wherein the additional oxygen-containing gas has been preheated to a temperature of from 100 to 700°C prior to being fed into the combustion chamber.

21. A process as claimed in claim 20, wherein the additional oxygen-containing gas has been preheated to a temperature of from 150 to 400°C prior to being fed into the combustion chamber.

22. A process as claimed in any one of claims 1 to 21, wherein the additional oxygen-containing gas has been premixed with additional water vapour prior to being fed into the combustion chamber.

23. A process as claimed in claim 22, wherein the amount of additional water vapour premixed with the additional oxygen-containing gas is from 5 to 20% by weight, based on the stoichiometric amount of water vapour.

24. A process as claimed in any one of claims 1 to 23, wherein the conical inlet nozzle has an internal diameter, at its opening into the

combustion chamber, of from 20 to 100 mm.

25. A process as claimed in claim 24, wherein the conical inlet nozzle has an internal diameter, at its opening into the combustion chamber, of from 50 to 70 mm.

26. A process as claimed in any one of claims 1 to 25, wherein the annular nozzle has a width within the range of from 0.2 to 2 mm.

27. A process as claimed in any one of claims 1 to 26, wherein combustion of the gas mixture is effected at a flame temperature within the range of from 800 to 1400°C.

28. A process as claimed in any one of claims 1 to 27, wherein cooling of the combustion chamber is effected by passing an oxygen-containing gas through a jacket around the combustion chamber, which gas is subsequently used as the oxygen-containing gas in the process, after further heating or cooling if necessary.

29. A process as claimed in claim 1, carried out substantially as described in any one of the examples herein.

30. Fume silica manufactured by a process as claimed in any one of claims 1 to 29.

31. Fume silica as claimed in claim 30, having an average particle size of less than 1 μm.

32. Fume silica as claimed in claim 30 or claim 31, having a BET specific surface area (as hereinbefore defined) within the range of from 50 to 450 m^2/g.

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